Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

LA-UR--86-3124

DE87 000145

TITLE: TERNARY SUPERCONDUCTORS

AUTHOR(S): A. L. Giorgi

SUBMITTED TO: 7th International Conference on Ternary Compounds

DISCLAIMER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

FORM NO 836 R4
ST NO 2629 5/81

TERNARY SUPERCONDUCTORS

A.L. GIORGI
Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

ABSTRACT

Ternary superconductors constitute a class of superconducting compounds with exceptional properties such as high transition temperatures (≈15.2 K), extremely high critical fields (H_{c2}>60 Tesla), and the coexistence of superconductivity and long-range magnetic order. This has generated great interest in the scientific community and resulted in a large number of experimental and theoretical investigations in which many new ternary compounds have been discovered. A review of some of the properties of these ternary compounds is presented with particular emphasis on the ternary molybdenum chalcogenides and the ternary rare earth transition metal tetraborides. The effect of partial substitution of a second metal atom to form pseudoternary compounds is examined as well as some of the proposed correlations between the superconducting transition temperature and the structural and electronic properties of the ternary superconductors.

INTRODUCTION

The early experimental work on superconducting materials concentrated to a large extent on binary and pseudobinary compounds and alloys and produced thousands of new superconducting materials with transition temperatures, T_c, ranging from a few millidegrees to the present maximum of 23.3 K for the binary Nb_3Ge. Interest in ternary superconductors really began about 14 years ago when Matthias et al.{1} reported the occurrence of relatively high superconductivity in some new ternary molybdenum sulfides which had recently been synthesized by Chevrel et al.{2}. A year later Odermatt et al. {3} reported that some of these new compounds were extremely high field superconductors with H_{c2} values more than 20 Tesla higher than any previously reported as shown in Fig. 1. These results were quickly followed by the discovery of superconductivity and magnetism in the rare-earth molybdenum sulfides by Fischer et al.{4} and the discovery of superconductivity or magnetism in a new class of rare earth rhodium tetraboride compounds $RERh_4B_4$ by Matthias et al.{5}. The very unusual and extremely interesting properties of these new materials generated great interest in ternary superconductors. As a result there have been a very large number of experimental and theoretical investigations which are still continuing today. Several new ternary superconductors have been discovered. A tabulation of some of the ternary superconductor with $T_c \geq$ 10 K is given in Table I.

Ternary superconductors are considered to include only those compounds which contain three different elements with each of the elements occupying unique positions in the crystal lattice. An examination of Table I shows that unlike the binary superconductors, the high T_c ternary superconductors are not dominated by a cubic symmetry but rather occur in a variety of crystal structures including even a modification of the copper molybdenum sulfide $Cu_{1.8}Mo_6S_8$ with a triclinic structure and a T_c≈11 K. Also most of the ternary superconductors contain a transition element and in many compounds the transition element groups together in "clusters" with the clusters occupying fixed positions in the crystal lattice. Both the ternary molybdenum sulfides (usually referred to as Chevrel phases) and the ternary rare earth rhodium tetraborides are cluster compounds.

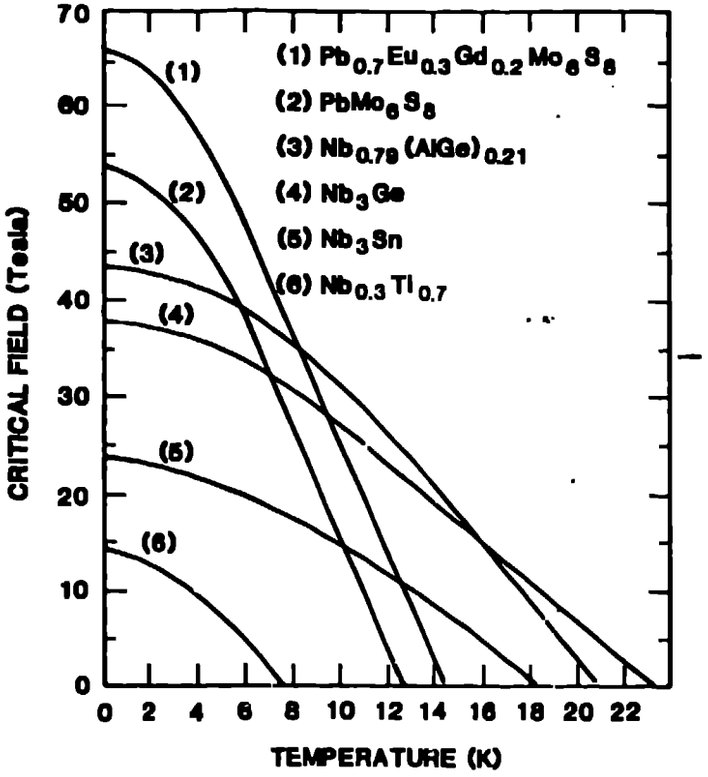

FIG. 1. Critical field vs temperature curves for Che phases as compared to other superconductors.

TABLE I. Some ternary superconductors with $T_c \geq 1$

COMPOUND	LATTICE TYPE	T_c(K)
$Pb_{0.92}Mo_6S_{7.5}$	RHOMBOHEDRAL	15.2
$Mo_6S_6I_2$	RHOMBOHEDRAL	14.0
$Mo_6S_6Br_2$	RHOMBOHEDRAL	13.3
$LiTi_2O_4$	CUBIC	13.7
$SnMo_6S_8$	HHOMBOHEDRAL	13.4
HfRuP	HEXAGONAL	11.8
$Zr_{0.61}Rh_{0.28}O_{0.11}$	CUBIC	11.8
$BaPb_{0.75}Bi_{0.25}O_3$	CUBIC	11.7
$LuRh_4B_4$	TETRAGONAL	11.7
YRh_4B_4	TETRAGONAL	11.3
$Cu_{1.8}Mo_6S_8$	RHOMBOHEDRAL	11.3
$LuRuB_2$	ORTHORHOMBIC	10.0
Mo_3Al_2C	CUBIC	10.0

METALLIC CLUSTERS

Metallic clusters with their metal-metal bonds have long been recognised as a structural feature of many inorganic compounds. These clusters are found to occur most often in compounds containing transition metals because of the d-electrons available for metal-metal bonding. The transition metals usually found in these cluster compounds are Nb, Mo, Rh, Re, Pt, and Au. Clusters occur in a wide variety of sizes and shapes depending on the oxidation state of the cluster transition metal. The clusters can be in the shape of pairs, triangles, squares, tetrahedra or octahedra and in the form of linear chains or zig-zag chains.

Two features of metallic clusters which are considered important are: 1) The spacing between the metal atoms in the cluster. This spacing is referred to as the intracluster distance, and 2) The spacing between the clusters called the intercluster distance. The intracluster distance is found to be very close to the interatomic cistance in the transition metal and remains essentially constant for different compounds. The intercluster distance on the other hand is much greater than the interatomic distance and varies for different compounds depending on the number and size of the metal cations. The physical properties of the cluster compounds are determined to a great extent by this intercluster distance. If this intercluster distance is between 10 and 20% larger than the interatomic diatance in the metal, weak metal-metal bonding still exists between the clusters and the cluster compound is metallic with a potential for superconductivity. When this intercluster distance is very large, no metal-metal bonds form between the clusters and the compounds are either insulators or semiconductors.

Chevrel Phases

The ternary molybdenum chalcogenides (Chevrel phases) have the general formula $M_xMo_6X_8$ in which M is anyone of a large number of metallic elements as shown in the periodic table in Fig. 2 and X is either S, Se, or Te. These compounds generally crystallize in the hexagonal-rhombohedral structure and can be considered as built up of M cations and Mo_6X_8 cluster units.

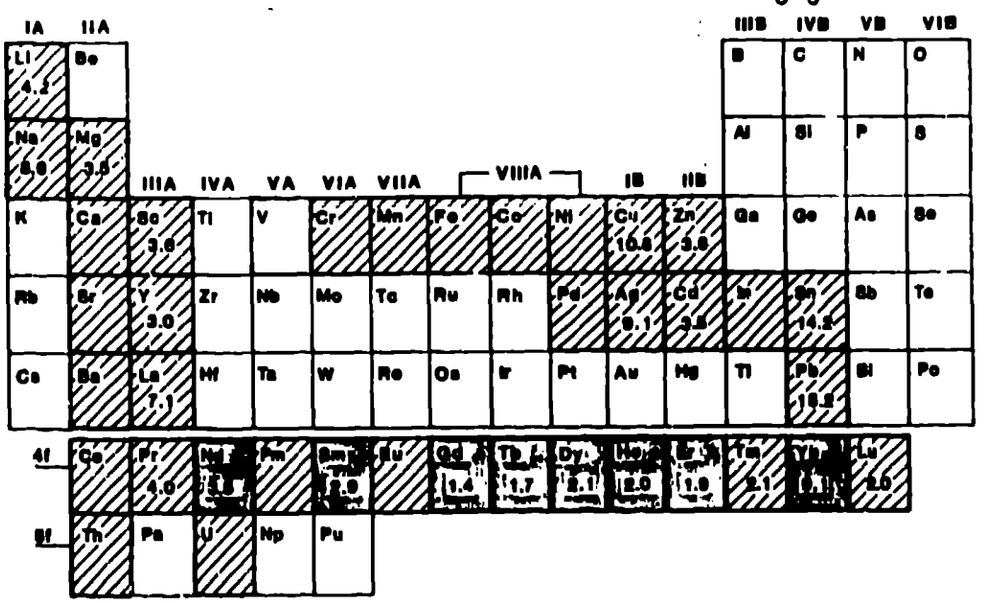

FIG. 2. The shaded elements all form the rhombohedral Chevrel phase. The numbers represent the T_c of the phases which are superconducting. The elements in the solid shaded rare earth group form Chevrel phases which are superconducting and also order magnetically.

The Mo_6X_8 unit, shown in Fig. 3, resembles a deformed cube with the 8 X atoms occupying the corners of the cube and enclosing the 6 Mo atoms which form an octahedron that is positioned so that the Mo atoms are at the center of each of the faces of the cube. With this arrangement the Mo clusters are well separated from each other in space so that the M elements can enter into the open channels between the Mo clusters. Since the chalcogen atoms separate the Mo atoms from the M atoms, the M-Mo distance is very large in these compounds.

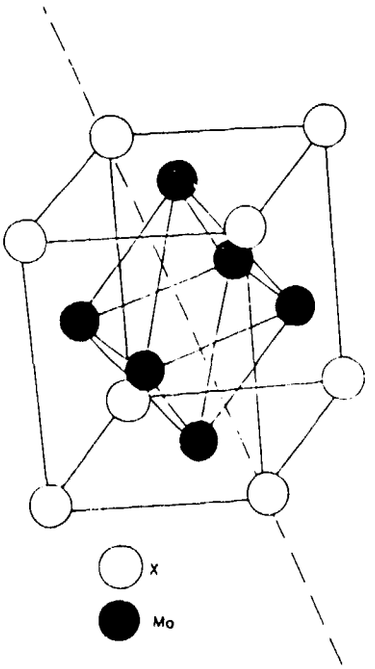

FIG. 3. The structure of the Mo_6X_8 cluster unit.

The compounds $M_xMo_6X_8$ are divided into two classes depending on the size of the metallic cation. When the metal M is a large cation (e.g. Pb, La, Sn) the value of x varies over a limited range and is close to unity. When M is a small cation (e.g. Cu, Co, Ni) the concentration of M may vary continuously over a wide range (e.g. from 1.6 to 4 for Cu and from 1.32 to 2 for Co and Ni). Associated with this wide homogeneity range is a low temperature structural phase transition from the rhombohedral structure to a triclinic structure that most of these compounds with small M undergo. This triclinic deformation is found to increase as the value of x for the M element increases and for the phase where M is Cr all compositions of $Cr_xMo_6S_8$ are triclinic. The range of compositions over which many of these Chevrel phases form is believed responsible for the varying T_c values reported by various investigators for the supposedly same compound. For example, reported values of T_c for the compound $PbMo_6S_8$ range from 11 to 15.2 K.

The superconductivity in the Chevrel phases has been shown to be due to the 4d electrons of the Mo clusters so the thought developed that if M were a magnetic element, because of the large M-Mo distance in these cluster compounds, the magnetic cation should have very little effect on the superconductivity. This might allow superconductivity and long-range magnetic order to coexist in the same compound. The discovery of the superconducting rare earth molybdenum chalcogenides $REMo_6X_8$ where RE is a rare earth element, presented investigators with a unique opportunity to study the interplay between superconductivity and long-range magnetic order. Previous studies had been limited to studying the effect of a small concentration of magnetic ions distributed in a random fashion throughout the crystal lattice. In the $REMo_6X_8$ compounds, the magnetic ions are arranged in the form of a regular sublattice. With the exception of Ce and Eu compounds the rare earth compounds $REMo_6X_8$ are all superconducting with T_c values above the magnetic

$(RE)Mo_6S_8$	T_c(K)	T_m(K)
$PrMo_6S_8$	3.5	<0.05
$NdMo_6S_8$	3.3	0.85
$SmMo_6S_8$	2.9	?
$EuMo_6S_8$	---	0.6
$GdMo_6S_8$	1.1	0.85
$TbMo_6S_8$	1.45	0.90
$DyMo_6S_8$	2.05	0.40
$HoMo_6S_8$	2.0	0.65
$ErMo_6S_8$	1.90	0.15
$TmMo_6S_8$	2.3	---
$YbMo_6S_8$	9.2	2.6
$GdMo_6Se_8$	5.6	0.75
$TbMo_6Se_8$	5.7	1.03
$ErMo_6Se_8$	6.0	1.07

TABLE II.

Superconducting, T_c, and magnetic, T_m, transition temperatures of the rare earth Chevrel phases.

these compounds is listed in Table II. The question now remained as to what happens when these superconducting compounds are cooled below their long-range magnetic ordering temperature. Recent results have shown conclusively that for the case where the rare earth ions order antiferromagnetically, superconductivity coexists with long-range antiferromagnetism. In the case of the compound $HoMo_6S_8$ it was found that as the compound is cooled it first undergoes a superconducting transition at 2.0 K and upon further cooling it becomes normal again at 0.65 K and shows long-range ferromagnetic ordering. Materials that exhibit this behavior are referred to as re-entrant superconductors.

Ternary Tetraborides

In 1977 Matthias et al.{5} reported the discovery of a new class of ternary rhodium borides which on cooling became either superconducting or ferromagnetic. These compounds have the general formula MRh_4B_4 where M is Y, Th or a rare earth element. As shown in Table III, when M is Y, Th, Nd, Sm, Er, Tm or Lu the compounds are superconducting with T_c values ranging from 2.5 to 11.8 K while the compounds in which M is Gd, Tb, Dy or Ho are ferromagnetic. Attempts to form this phase with the elements Sc, La, Ce, Pr and Yb were unsuccessful.

A comparison of these ternary rhodium tetraborides with the Chevrel phases reveals that they are similar in many respects:

1. The tetraborides are cluster compounds and contain Rh_4B_4 units consisting of interpenetrating Rh and B tetrahedra. See Fig. 4.
2. The intracluster distance Rh-Rh is almost equal to the interatomic distance in Rh metal and is much smaller than the intercluster distance.
3. The superconducting tetraborides have relatively high T_c values approaching 12 K.
4. The rare earth ions form an ordered sublattice in the crystal structure.
5. One of the compounds, $ErRh_4B_4$, is a re-entrant type superconductor.

TABLE III. Superconducting, T_c, and magnetic, T_m, transition temperatures of $(RE)Rh_4B_4$ compounds.

$(RE)Rh_4B_4$	T_c(K)	T_m(K)
YRh_4B_4	11.3	----
$NdRh_4B_4$	5.36	----
$SmRh_4B_4$	2.51	----
$ErRh_4B_4$	8.55	----
$TmRh_4B_4$	9.86	----
$LuRh_4B_4$	11.8	----
$ThRh_4B_4$	4.34	----
$GdRh_4B_4$	----	5.62
$TbRh_4B_4$	----	7.08
$DyRh_4B_4$	----	12.0
$HoRh_4B_4$	----	6.56

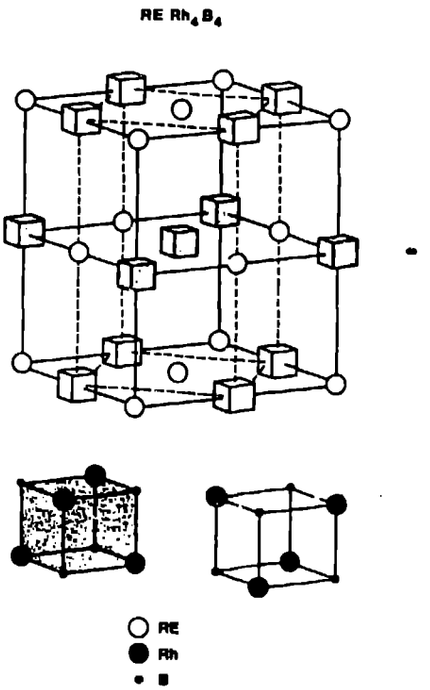

FIG. 4. Idealized crystal structure of the $RERh_4B_4$ compound.

The main differences between the ternary rhodium tetraborides and the Chevrel phases would include:

1. The crystal symmetry of the MRh_4B_4 compounds is tetragonal.
2. Whereas the metallic radii of the M atom can vary over wide limits in the Chevrel phase, in the MRh_4B_4 compounds only M atoms with metallic radii between 1279 and 1.82 Å will form the phase
3. The rather abrupt change from superconductivity to magnetism back to superconductivity as the M atom is replaced going across the rare earth series from Nd to Lu.

Pseudoternary Systems

Pseudoternary compositions are formed by the substitution of various amounts of a second metal atom in either of the two crystal sites occupied by the metal atoms of the ternary compound. Such compositions have generated a great amount of interest among investigators because of the added dimension these compositions provide in the study of the interplay between superconductivity and long-range magnetic order. Pseudoternaries permit the investigation of competing interactions which would not be possible in the pure ternary compounds. Pseudoternary systems of both the Chevrel phases and the rare earth rhodium tetraborides have been studied extensively and often unexpected phenomena has been observed.

There are two types of $RERh_4B_4$ pseudoternaries which have been prepared and studied. In the first type various amounts of a second rare earth is substituted in the crystal site occupied by the RE metal. The second type involves substituting various amounts of another transition metal in the crystal site occupied by the Rh atoms. Numerous studies of both types of pseudoternary systems have been carried out and the low temperature phase diagrams depicting the magnetic and superconducting regions determined.

The pseudoternary system $(Er_{1-x}Ho_x)Rh_4B_4$ investigated by Johnston et al.{6} is a particularly interesting system of the first type since it in-

volves superconductivity and two kinds of magnetic interactions which are all competing with each other. The transition from the re-entrant superconductivity observed in the $ErRh_4B_4$ end member to the ferromagnetism reported for the other end member $HoRh_4B_4$ is investigated by studying the variation of T_c and T_m as a function of the composition over the entire range of $0<x<1.0$. The low temperature phase diagram for this pseudoternary system is given in Fig. 5. An interesting example of a pseudoternary system of the second type is the system $Tb(Rh_{1-x}Ir_x)_4B_4$ which was investigated by Ku et al.{7}. The low temperature phase diagram of this system is given in Fig. 6. The end members of this system are not superconducting and have different structures. One end member $TbRh_4B_4$ crystallizes in the rhombohedral $CeCo_4B_4$-type structure (phase A) and is ferromagnetic. The other end member $TbRh_4B_4$ is also ferromagnetic and crystallizes in the $NdCo_4B_4$-type structure. Although neither end member is superconducting, superconductivity occurs in the phase A region of the pseudoternary system $Tb(Rh_{1-x}Ir_x)_4B_4$ over the compositional range of $0.25<x<0.72$.

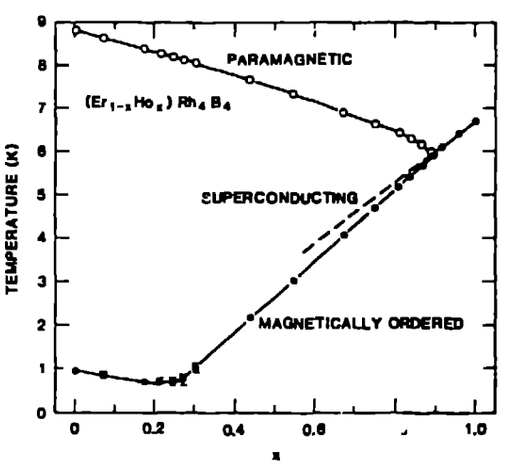

FIG. 5. Low temperature phase diagram of the $(Er_{1-x}Ho_x)Rh_4B_4$ system.

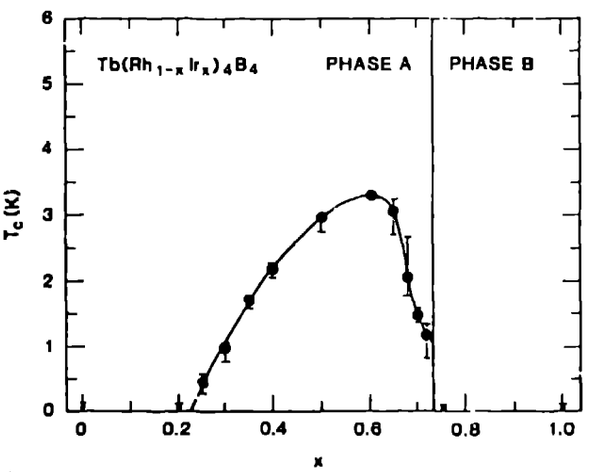

FIG. 6. Low temperature phase diagram of the $Tb(Rh_{1-x}Ir_x)_4B_4$ system.

CORRELATIONS

Various correlations between T_c and the electronic and structural properties of binary superconductors have been proposed over the years. A few of the more popular ones include the effect on T_c of: crystal symmetry, valence electrons per atom, atomic disorder, lattice instabilities and structures. Similar correlations are being suggested for the ternary superconductors. One of the earliest correlations was proposed by Marezio et al.{8}. They found that T_c and the volume of the cell were closely related with the highest T_c values occurring in the phases with the larger cell volumes. Other suggestions include T_c and lattice instabilities and T_c and the axial c/a ratio. Attempts to correlate T_c with the number of valence electrons per atom were unsuccessful. A modification of this method by Yvon and Pooli{9} has received favorable results. They consider only the transition metal (e.g. Mo) and count as valence electrons those which are left on the cluster after the octet of the 8 chalcogen atoms are completed. The resulting number, called cluster VEC, is found to relate well with T_c. VEC values vary from 20 to 24 per cluster. The highest T_c values occur for VEC values of 22 and fall sharply for VEC values above and below this value.

References

1. B.T. Matthias, M. Marezio, E. Corenzwit, H.S. Cooper, H.E. Barz, Science 175, 1465 (1972).
2. R. Chevrel, M. Sergent, J. Prigent, J. Sol. State Chem. 3, 515 (1971).
3. R. Odermatt, Ø. Fischer, H. Jones, G. Bongi, J. Phys. C7, L13 (1974).
4. Ø. Fischer, A. Treyvard, R. Chevrel, M. Sergent, Sol. State Commun. 17, 721 (1975).
5. B.T. Matthias, E. Corenzwit, J.M. Vandenberg, H.E. Barz, Proc. Nat'l Acad. Sci. USA 74, 335 (1977).
6. D.C. Johnston, W.A. Fertig, M.B. Maple, B.T. Matthias, Sol. State Commun. 26, 141 (1978).
7. H.C. Ku, S.E. Lamberth, M.B. Maple, in Superconductivity in d- and f-Band Metals 1982, edited by W. Buchel and W. Weber (Kernforschungszentrum Karlsruhe, 1982), p. 231.
8. M. Marezio, P.D. Dernier, J.P. Remeika, E. Corenzwit, B.T. Matthias, Mat. Res. Bull. 8, 657 (1973).
9. K. Yvon and A. Pooli, Sol. State Commun. 24, 41 (1977).